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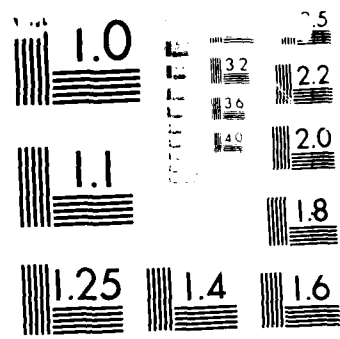
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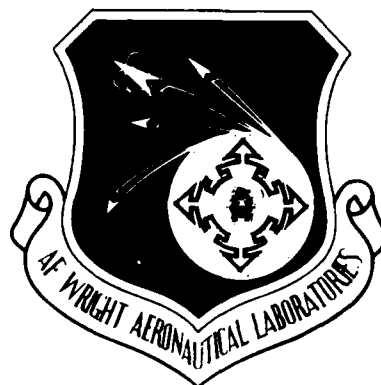
S. J. Bai
University of Dayton
Research Institute
300 College Park Avenue
Dayton, OH 45469

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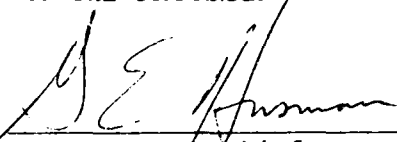
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T. E. HELMINIAK
Work Unit Scientist


R. L. VAN DEUSEN
Chief, Polymer Branch
Nonmetallic Materials Division

FOR THE COMMANDER


G. E. HUSMAN, Chief
Nonmetallic Materials Division

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FOREWORD

This report was prepared by the University of Dayton Research Institute, Nonmetallic Materials Division, Polymer Group. This work was initiated under U.S. Air Force Contract #F33615-84-C-5020, "Exploratory Development on Polymeric Materials for Advanced Aircraft and Aerospace Vehicles". It was administered under the direction of the Materials Laboratory, Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Dr. T. E. Helminiak as the Contract Monitor. The author was Dr. S. J. Bai, University of Dayton Research Institute, with Dr. Donald R. Wiff as the Principal Investigator.

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TABLE OF CONTENTS

	PAGE
1. INTRODUCTION	1
2. NEUTRON SCATTERING	3
3. NETWORK PREPARATION	4
4. SMALL-ANGLE NEUTRON SCATTERING MEASUREMENTS	6
5. RESULTS AND DISCUSSIONS	9
6. CONCLUSIONS	12
REFERENCES	14

LIST OF ILLUSTRATIONS

FIGURE		PAGE
1	Wide-angle X-ray scattering on epoxy network of EPON 825 cured with a mixture of half of the stoichiometric amounts of mPDA and mPDAd ₄	19
2	Small-angle neutron scattering on labeled (●) and unlabeled (○) epoxy networks of X-22 cured with stoichiometric amounts of amines	20
3	Small-angle neutron scattering on labeled (●) and unlabeled (○) epoxy networks on EPON 825 cured with stoichiometric amounts of amines	21

LIST OF TABLES

TABLE		PAGE
1	Neutron scattering factors for the cured epoxy network of DGEBA/MPDA	17
2	Neutron scattering measurement configurations applied for the DGEBA/MPDA networks at the Oak Ridge National Laboratory (ORNL) and the National Bureau of Standards (NBS)	18

1. INTRODUCTION

Epoxy resins are generally reacted with curing agents to form thermoset networks which are widely used in structural applications primarily as a matrix in advanced composite materials. The microstructure of the epoxy networks has attracted considerable interest. Extensive investigations have focussed on the existence of heterogeneities in and the distribution of crosslinks throughout the epoxy network.¹⁻¹³

Many studies have been reported on epoxy networks where a distinct second phase or heterogeneity has been detected. Small-angle X-ray scattering (SAXS),¹ nuclear magnetic resonance (NMR),² electron paramagnetic resonance (EPR),³ and glass transition temperature (T_g)⁴ measurements reveal a second phase which is attributed to a heterogeneous microstructure in the 100 to 1000 Å range. Direct imaging of the epoxy network by electron microscopy (EM) of ultramicrotomed sections,⁵ replicas of sections,⁶ unetched and etched fracture surfaces,⁷⁻⁹ shows a distinct nodular structure which is 100-600 Å in size. EM examinations of selectively reacted networks, either by plasma-etching of the fracture surface or by chemical staining, have further identified the nodules as being comprised of high crosslink density with a broad size distribution, predominantly in the 100 to 300 Å range, in a matrix of relatively low crosslink density. A most recent detailed EM study¹⁰ of an epoxy network of diglycidyl ether of bisphenol A cured with meta-phenylene diamine produces further evidence for the existence of these heterogeneities. It demonstrates that the size of these heterogeneities varies with the system stoichiometry and cure conditions. The stoichiometric amine-epoxy composition produces the

smallest heterogeneity with the size increasing with either an excess of amine or epoxy.

Equally convincing, there is another school of evidence which suggests that the cured epoxy networks are homogeneous and do not have aggregations of crosslinks into nodules. It is considered that evidence of inhomogeneity in the network from SAXS, NMR, and EPR fails to correlate the inhomogeneities with aggregations of crosslinks because either the technique (SAXS) is inadequate to identify the crosslink aggregations or the techniques (NMR, EPR) examine only the local molecular behavior instead of larger scale nodular morphology. Measurements of T_g may be explained by the nonequilibrium character of the thermodynamic properties, and not necessarily by the formation of heterogeneities of crosslinks.^{11,12} Nodular morphology of the epoxy network obtained from EM is also questioned. Mainly, similar inhomogeneities have been observed by EM on bulk atactic polystyrene and poly(methyl methacrylate) which are linear polymers and contain no crosslinks.¹³

In this study, we focus our efforts on the crosslink distribution of a selected epoxy network of high crosslink density and on the existence of the nodular morphology which was reported to have a size predominantly in the 100 to 300 Å range.¹⁰ Our approach is to apply neutron scattering on an epoxy network cured stoichiometrically with isotope-labeled curing agents (this network reportedly generates the smallest nodules).¹⁰ We believe that this application of neutron scattering provides a unique nondestructive means to study definitively the distribution of crosslinks in the epoxy network.

2. NEUTRON SCATTERING

Scattering of neutrons is due to neutron-nucleus interactions. The neutron scattering cross sections of nuclei vary in a non-systematic manner, unlike X-ray scattering cross sections which increase with atomic number. A good example is the distinct difference in neutron cross sections of ^1H and ^2D . Hence, neutron scattering on isotope-labeled system where ^1H is substituted with ^2D (which preserves identical chemical characteristics of the system) provides a unique approach in the study of hydrogen-containing systems, such as polymers.

Neutron scattering intensity, like all other scattering intensities, is related to a simple spatial correlation function in the following manner. The elastic intensity

$$\begin{aligned} I^{\text{el}}(\underline{Q}) &\propto \langle \left| \sum_j a_j e^{i\underline{Q} \cdot \underline{r}_j} \right|^2 \rangle \\ &= \langle \sum_{i,j} a_i a_j e^{i\underline{Q} \cdot (\underline{r}_i - \underline{r}_j)} \rangle \end{aligned} \quad (1)$$

where a_i is a quantity related to the scattering power of the i -th scattering unit at \underline{r}_i ; $\underline{Q} \equiv \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right) \hat{\underline{Q}}$ for elastic scattering, where θ is the scattering angle; the bracket indicates ensemble average over all the accessible states of the system.

Akcasu et al.¹⁴ and Williams et al.¹⁵ have formulated the coherent intensity, $I_{\text{coh}}^{\text{el}}$, of Eq. (1) for a deuterium-labeled system, which can be described as

$$I_{\text{coh}}^{\text{el}}(\underline{Q}, C) = N C(1-C) |b_{\text{D}} - b_{\text{H}}|^2 [S_{\text{S}}(\underline{Q}) + A(C) S_{\text{T}}(\underline{Q})] \quad (2)$$

where

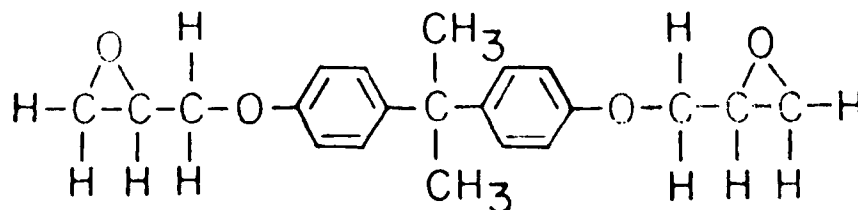
$$S_S(Q) = \frac{1}{N} \left\langle \sum_{k,l} e^{iQ \cdot (r_k - r_l)} \right\rangle$$

$$S_T(Q) = \left\langle \sum_{i,j} e^{iQ \cdot (r_i - r_j)} \right\rangle$$

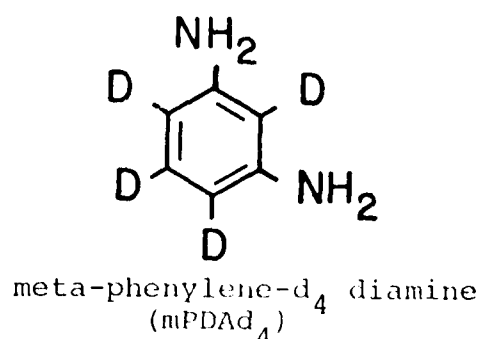
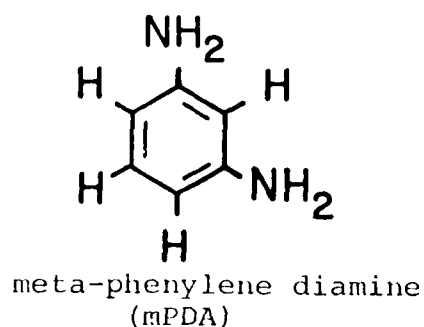
and C is the percentage of labeling, N is the number of the labeling component, b_D and b_H are the coherent scattering lengths (their values will be given later) of deuterated unit and of protonated unit, respectively. $S_S(Q)$ is the form factor of the spatial correlation of the labeling component only (k and l sum over the units of the labeling component). $|b_D - b_H|^2$ is called the contrast factor resulting from the deuterium-hydrogen substitution. $\Lambda(C)$ is a constant which is related to the percentage of labeling in the whole system. $S_T(Q)$ is the form factor of the total correlation of the system (i and j sum over the whole system). For X-ray scattering the isotope labeling concentration C is considered to be zero or one, the scattering intensity is actually a measurement of $S_T(Q)$.

3. NETWORK PREPARATION

In order to maximize the possible aggregation and the amount of crosslinks per unit volume, we elected to use the smallest molecule of the epoxy resin based on diglycidyl ether of bisphenol A (DGEBA) having the following chemical structure



Samples of this DGEBA resin were obtained as EPON 825 from Shell Chemical Co. and a recrystallized resin designated as X-22. Liquid chromatographic analyses have shown that both resins are monodisperse in molecular weight. They are liquids of high viscosity at room temperature with an epoxide equivalent of 170. The curing agent was meta-phenylene diamine (mPDA), an aromatic amine which is a solid at room temperature with a melting point of 68°C. For neutron measurements in determining crosslink distribution of a cured epoxy network, we used meta-phenylene-d₄ diamine (mPDAd₄) as the labeled component. With complete deuterium labeling on the phenylene of mPDA we can (1) preserve identical curing kinetics of the amine-epoxy reaction, (2) provide a definitive labeling for neutrons to examine the distribution of crosslinks in the epoxy network. The chemical structures of the curing agents are given below:



The epoxy resin and the curing agent were heated or melted separately in an oven at 75°C. The curing agent was then mixed with the epoxy resin and deaerated. At the same time vigorous mixing took place. The mixture was cast in silicon rubber molds into discs of 2 cm diameter. A thermal curing cycle of two hours at 75°C followed by two hours at 125°C was then applied. The cured samples were cooled slowly to room

temperature by ambient conditions. In order to determine the crosslink distribution, by measuring $S_S(Q)$ in Eq. (1), we have prepared independently two sets of samples of EPON 825 and X-22 each cured with stoichiometric amounts of curing agent. Use of two epoxy resins with identical chemical structure was designed to demonstrate the reproducibility of our sample preparation and the consistency of the measurement data. The stoichiometric amount for mPDA is 15.88 and for mPDAd₄ is 16.47 weight fraction of curing agent per hundred parts of DGEBA resin (phr). The curing agent compositions were mPDA at 15.8 phr (i.e. C=0.0) and a mixture of mPDA and mPDAd₄ at half of their respective stoichiometric amounts to have the DGEBA resin still cured with stoichiometric amount of the amine curing agent, but with half of the curing agents deuterium-labeled (i.e. C=0.5). Infrared absorption spectroscopy has established that the epoxy networks have degree of cure above 94 percent.

Neutron scattering intensity difference between the labeled network and the unlabeled network should be an indication of the distribution of the labeling component. In this case, it is precisely the distribution of crosslinks in the epoxy network.

4. SMALL-ANGLE NEUTRON SCATTERING MEASUREMENTS

As shown in Equation (1), the scattering intensity is related to the ensemble average of all the accessible states of the system. Because of the nature of neutron-nucleus interactions in neutron scattering, the ensemble average over all the accessible nuclear spin states will generate incoherent scattering intensity I_{incoh} . The total intensity of scattered neutrons can be written as

$$I = T_n K (I_{\text{coh}} + I_{\text{incoh}}) + \text{system noise} \quad (3)$$

where T_n is the transmission factor of the sample;

$K \equiv I_0 \cdot \Delta\Omega \cdot \Delta t \cdot \epsilon(Q)$; I_0 is the incident neutron flux; $\Delta\Omega$ is the solid angle of a detector element; Δt is the exposure time; and $\epsilon(Q)$ is the efficiency of the detector element, which is a function of λ and θ .

For small-angle neutron scattering (SANS) on a deuterium-labeled system, the elastic coherent scattering intensity given in Eq. (2) is an adequate expression. The coherent scattering intensity, I_{coh} , is then written as

$$I_{\text{coh}}(Q, C) = N C(1-C) |b_D - b_H|^2 S_S(Q) + A(C) S_T(Q) \quad (4)$$

The incoherent scattering intensity can be simply expressed as the sum of contributions from each nucleus,

$$I_{\text{incoh}}(C) = \frac{1}{4\pi} \left\{ \sum_i \sigma_i^{\text{inc}} \right\} \quad (5)$$

where σ_i^{inc} is the incoherent scattering cross section of the i -th nucleus. It should be noted that σ_i^{inc} is a constant and the incoherent intensity is distributed uniformly over 4π solid angle. In Table 1, we list the scattering factors for all the nuclei of the network of DGEBA/MPDA. It is obvious that in the network ^1H is the predominant contributor in scattering neutrons incoherently. It should also be pointed out that when MPDA in the network is substituted with MPDA₄ to definitively label the crosslinks the incoherent intensity decreases, i.e. $I_{\text{incoh}}(0.5) < I_{\text{incoh}}(0.0)$.

For long wavelength neutrons, the phenylene of MPDA can be treated as a point scatterer. The coherent scattering length b

is the sum of coherent scattering lengths of the atoms in the scattering unit. For the labeling component of the epoxy network,

$$b_D = 6.658 \times 10^{-12} \text{ cm},$$

$$b_H = 2.602 \times 10^{-12} \text{ cm},$$

and the contrast factor $|b_D - b_H|^2 = 16.45 \text{ barn/MPDA}$.

Then, N is the number of curing agent molecules or, equivalently, of crosslinks in the epoxy network.

SANS measurements were performed at the National Center for Small-Angle Scattering Research (NCSASR) at the Oak Ridge National Laboratory (ORNL). Two independent sets of network samples were measured on two spectrometer configurations (one before and one after the reblanketing of the High Flux Isotope Reactor that happened in 1983) with sample to detector distances (SDD) of 2.0 m and 4.3 m. This was designed to cover an angular region equivalent to a real-space distance up to 400 \AA to encompass the crosslink aggregations which have been claimed by electron microscopic evidence. Even though we are going to report only the neutron scattering results taken on the NCSASR facility, it should be mentioned that one set of the network samples was also sent to the National Bureau of Standards (NBS) for preliminary measurement purposes. The measurement configurations for all SANS on epoxy network are summarized in Table 2. The system noise of each measurement configuration was determined and subtracted. The $T_n K$ factor was removed with measured transmission values and with SANS measurements of H_2O which scatters neutrons incoherently. As shown in Eq. (3), the net intensity is then composed of contributions only from $(I_{\text{coh}} + I_{\text{incoh}})$.

5. RESULTS AND DISCUSSIONS

In the application of SANS on isotope-labeled systems, it is necessary to address the problem of "isotope segregation," i.e. the deuterium-labeled component aggregates together and is not distributed statistically. This kind of phase separation casts serious doubt on measured $S_S(Q)$ and the interpretation extracted from it. This is particularly true in systems involving co-crystallization of the labeled and the unlabeled components. One of the well-known examples is SANS on polyethylene.¹⁶⁻¹⁸ It becomes necessary to demonstrate that similar concern is not warranted for our epoxy networks.

Figure 1 is a wide-angle X-ray scattering (WAXS) intensity profile for the labeled EPON 825 network, which shows an intense signal at $\sim 19^\circ$ (with Cu $K\alpha$ radiation) and is attributed to be the diffuse "halo" of scattering from a typical amorphous system, like atactic polystyrene. However, unlike the ones from semi-crystalline polyethylene, this WAXS spectrum does not have any lattice diffraction intensity which is related to the existence of crystalline structure. Because no lattice structure has been detected, the known amorphous nature of the cured epoxy network is proven here for our particularly labeled DGEBA/MPDA networks. Therefore, a large degree of isotope segregation of MPDA and MPDA_{d4} is unlikely to have happened. It is reasonable to consider that the labeled MPDA_{d4} is distributed statistically throughout the network like other labeled components in completely amorphous systems.^{14,19}

Net SANS intensities of two different sets of DGEBA/MPDA networks are presented in Figures 2 and 3 for the two measurement configurations at NCSASR for a combined Q-region from 0.016 to 0.220 \AA^{-1} which is equivalent to real-space distances from 400 to 30 \AA . The two measurement configurations were also selected to overlap an extended Q-region to resolve better the low-Q behavior of SANS intensities in Figure 2 and to show the consistency of the measurements. Within experimental error, the general feature of the intensities can be approximated as being constant over the entire Q-region, and the labeled networks indeed have excess intensity, i.e. $I(Q, 0.5) > I(Q, 0.0)$.

The reduction of these net SANS intensities, of $I_{\text{coh}} + I_{\text{incoh}}$, in obtaining $S_S(Q)$ can be described as follows:

(1) I_{coh} contains contributions from $S_S(Q)$, from the correlation of the labeling component only, and $S_T(Q)$, from the total correlation of the whole system. As indicated before $S_T(Q)$ can be obtained by X-ray scattering. We have examined the epoxy networks with SAXS using a pin-hole camera and a high resolution slit-source Kratky camera. The X-ray intensities over an extended Q-region ($0.005 < Q < 0.40 \text{ \AA}^{-1}$) are negligible. This shows an insignificantly small $S_T(Q)$. In addition, our particular labeling scheme, by replacing half the stoichiometric amount of MPDA with MPDA₄, and the use of monodisperse DGEBA molecules allow us to consider the network that on the average (as MPDA₄ is distributed statistically) one of the $28 \text{ }^1\text{Hs}$ in the repeat unit of the network was replaced by ^2D . Moreover, the substitution was done precisely on the phenylene of MPDA to reflect the

distribution of crosslinks throughout the epoxy network. This slight modification in the repeat unit of the network suggests that $A(0.5) \approx A(0.0)$. Consequently, in considering the excess of coherent intensity between labeled and unlabeled networks, the contribution from total correlation of the network is negligible, i.e. $A(0.5)S_T(Q) - A(0.0)S_T(Q) = 0$. In other words, the net SANS intensity of the unlabeled network is $I_{inc}(0.0)$.

(2) As shown in Table 1, the substitution of 1H by 2D should decrease the incoherent scattering intensity which is independent of θ , i.e. $I_{incoh}(0.0) > I_{incoh}(0.5)$. For the network of monodisperse DGEBA molecules cured with stoichiometric amounts of mPDA, it can be calculated that in substituting one of the 28 1H s by 2D in the repeat unit of the network, the incoherent scattering intensity decreases by about 3.5 percent which is within the uncertainty of the SANS measurement and means experimentally $I_{incoh}(0.0) \approx I_{incoh}(0.5)$.

Owing to insignificant contribution from $A(C)S_T(Q)$ and similar contributions for I_{incoh} , we can say certainly that the difference in net intensity of $I(Q,0.5) - I(Q,0.0)$, as shown in Figures 2 and 3, can only be attributed to $S_S(Q)$ and can be approximated as a positive constant. The interpretation of $S_S(Q) = c > 0.0$ is straightforward, that the spatial distribution which is a Fourier transform of $S_S(Q)$ is required also to be a positive constant over a region from 30 to 400 Å. Since $S_S(Q)$ is due to the excess intensity from the labeling component, this further shows that the labeling component is distributed uniformly throughout the space. The deuterium-labeling has been selectively

applied on the phenylene of the amine curing agent and is a true reflection of the crosslinking sites, we thus establish that the crosslinks are uniformly distributed throughout the network.

In summary, WAXS demonstrates that the deuterium-labeled networks of DGEBA/MPDA is a completely amorphous system. SANS on the unlabeled networks and SAXS on the networks over an extended Q-region show negligible intensity. In other words, the intensity due to total correlation of the system is zero, and no significant heterogeneities have been observed. Application of SANS on epoxy resins cured with deuterium-labeled MPDA does have a constant excess intensity over the unlabeled epoxy network. This constant excess intensity can only be attributed to a constant spatial correlation of the labeling component (i.e. the amine curing agent) over a range of 30 to 400 Å. Owing to the unique and definitive deuterium-labeling of the phenylene of the MPDA curing agent, we can say that within experimental error the crosslinks are distributed uniformly throughout the epoxy network. The network morphology of aggregation of crosslinks into domains, of sizes predominantly in the 100 to 300 Å range, needs to be reexamined.

6. CONCLUSIONS

Crosslink distribution of the network was studied by SANS on epoxy resins cured with deuterium-labeled curing agent. A complete deuterium-hydrogen substitution was applied precisely on the phenylene of the MPDA curing agent. Deuterated and protonated MPDA was cured with a monodisperse DGEBA resin with

the smallest molecular weight to enhance the crosslink density. The labeled networks do produce a constant excess SANS intensity which can only be attributed to the uniform distribution of the labeling component of the network, i.e. the amine curing agent. Consequently, this nondestructive approach clearly demonstrates that the crosslinks are distributed uniformly throughout the epoxy network.

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Table 1. Neutron scattering factors for the cured epoxy network of DGEBA/MPDA.

NUCLEUS	SPIN	$b(10^{-12}\text{cm})$	$\sigma^{\text{coh}}(\text{barn})$	$\sigma^{\text{inc}}(\text{barn})$
^1H	1/2	-0.347	1.76	79.24
^2D	1	0.667	5.59	2.01
^{12}C	0	0.665	5.95	—
^{14}N	1	0.936	11.01	0.46
^{16}O	0	0.580	4.23	—

Table 2. Neutron scattering measurement configurations applied for the DGEBA/MPDA networks at the Oak Ridge National Laboratory (ORNL) and the National Bureau of Standards (NBS). ^3He position sensitive detectors (PSD) were used.

	ORNL - NCSASR	NBS
λ	4.75 Å	5.10 Å
SDD	2.00 M, 4.30 M	3.60 M
DET	PSD (64 x 64 cm ²)	PSD (64 x 64 cm ²)
	$0.016 < Q < 0.220 \text{ Å}^{-1}$	$0.020 < Q < 0.200 \text{ Å}^{-1}$

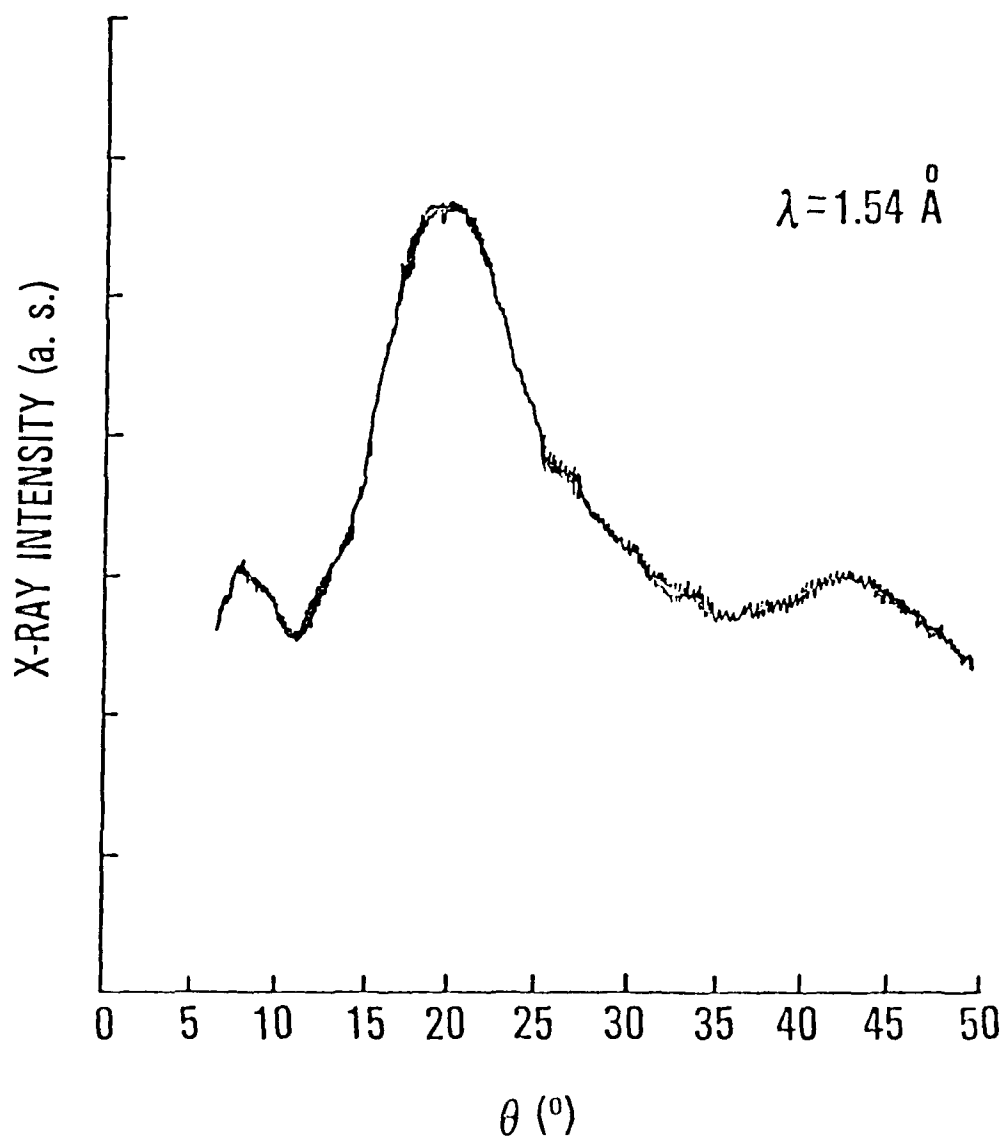


Fig. 1. Wide-angle X-ray scattering on epoxy network of EPON 825 cured with a mixture of half of the stoichiometric amounts of mPDA and mPDA₄.

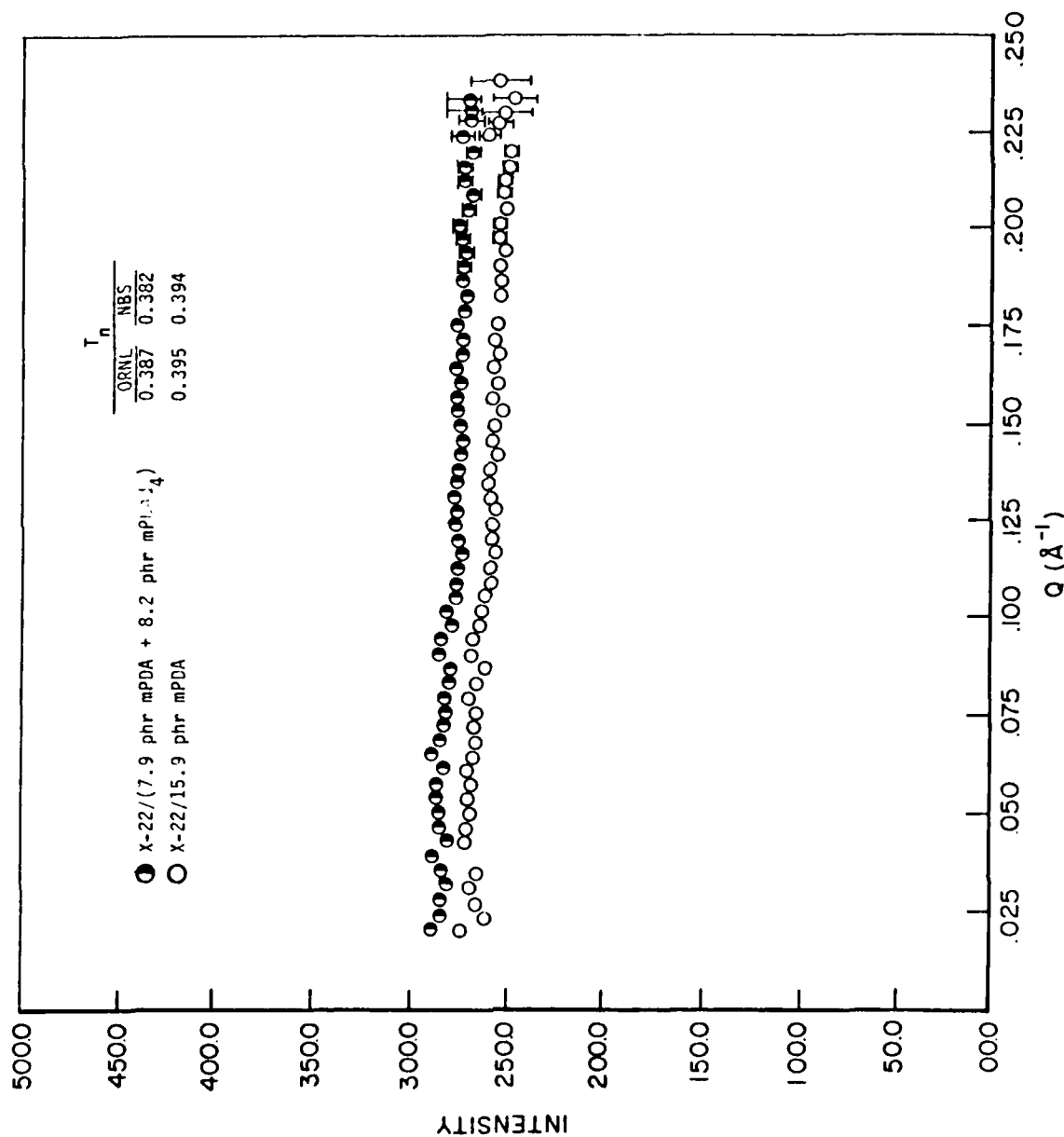


Fig. 2. Small-angle neutron scattering on labeled (\bullet) and unlabeled (\circ) epoxy networks of X-22 cured with stoichiometric amounts of amines. Results were obtained on the ORNL 60-m neutron scattering facility with a sample to detector distance (SDD) of 2.0m.

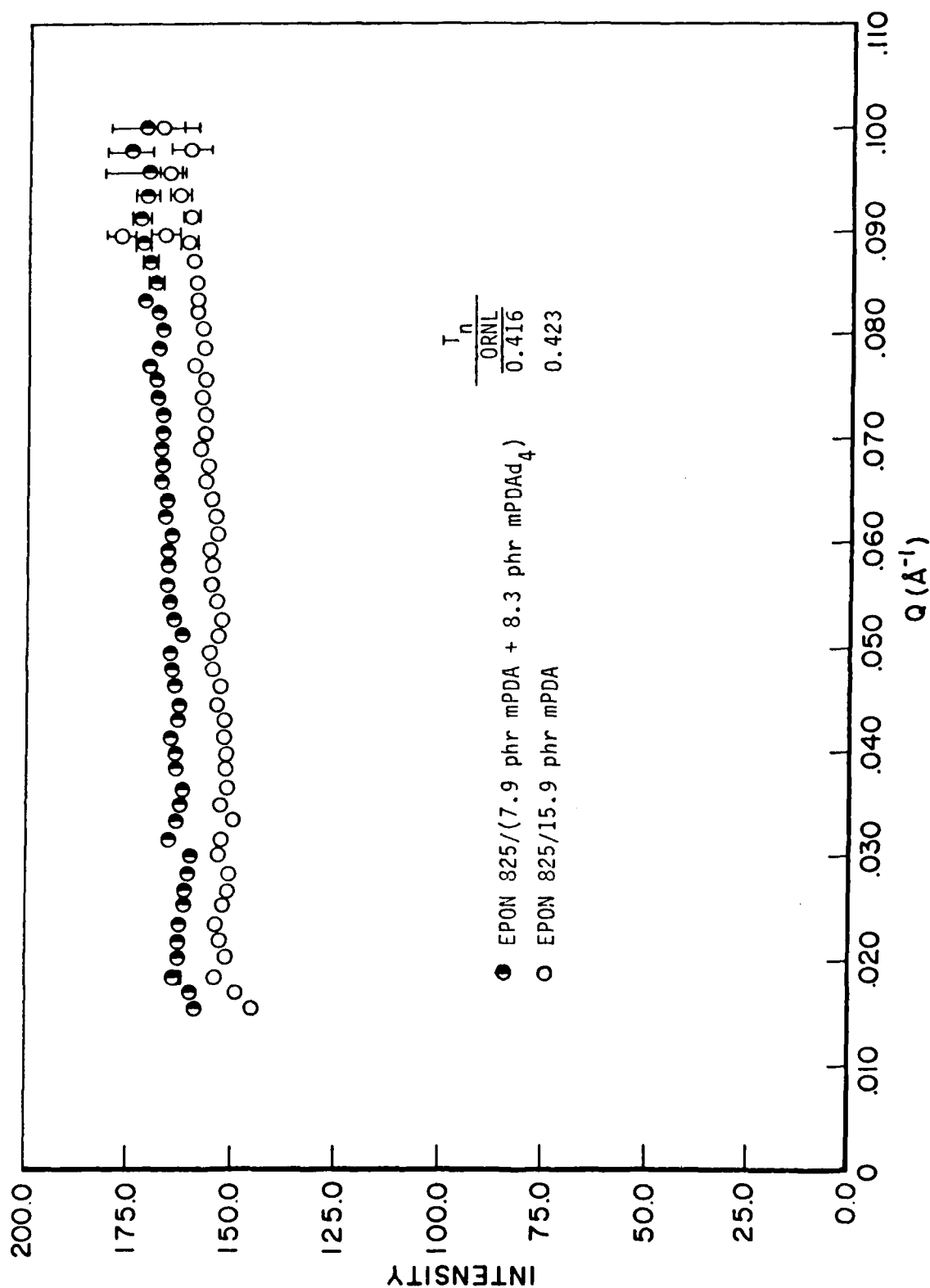


Fig. 3. Small-angle neutron scattering on labeled (●) and unlabeled (○) epoxy networks on EPON 825 cured with stoichiometric amounts of amines. Results were obtained on the ORNL 30-m neutron scattering facility with a sample to detector distance (SDD) of 4.3m.

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